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(54) Title: ZIRCONIA-BISMUTH OXIDE GRADED ELECTROLYTE
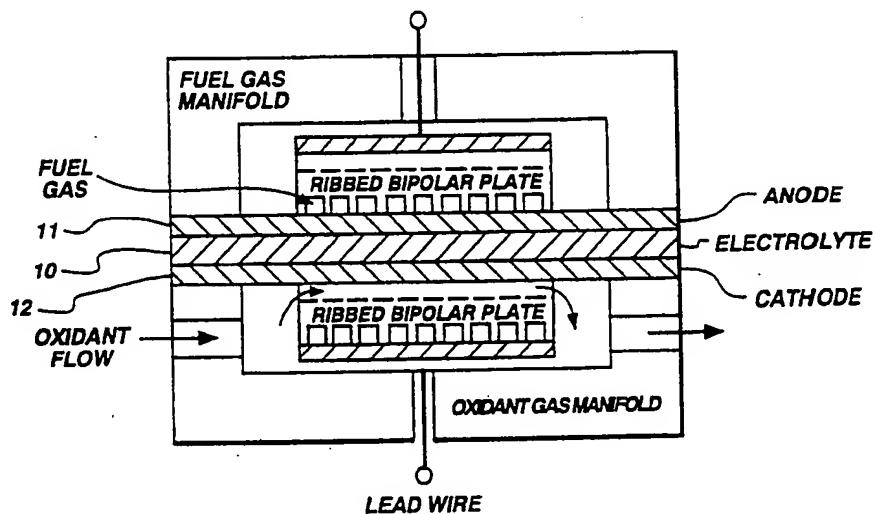
PLANAR CONFIGURATION
SOLID OXIDE FUEL CELL

(57) Abstract

A graded electrolyte of zirconia and bismuth oxide containing proposed surface regions one of which is rich in zirconia, the other rich in bismuth oxide is disclosed. The strength and reduction resistance of zirconia is combined with the high ionic conductivity of bismuth oxide to form a superior oxygen ion-conducting electrolyte (10) which is especially useful in fuel cells. The electrolyte (10) is located between an anode (11) and a cathode (12).

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ZIRCONIA-BISMUTH OXIDE GRADED ELECTROLYTE

BACKGROUND OF THE INVENTION

5   This invention relates to oxygen ion conducting
electrolytes and particularly to zirconia/hafnia electro-
lytes used in solid oxide fuel cells.

State of the Art: Solid oxide fuel cells
10   (SOFCs) are well known in the art with many different
structures having been employed. However, SOFCs,
regardless of structure and materials of construction,
employ a solid electrolyte which conducts oxygen ions, is
generally unaffected by oxidizing or reducing conditions
15   and can withstand temperatures of at least 600°C.

Typical fuel cells are described in the
following U.S. Patents: U.S. Patent No. 4,476,196 by
Poeppel et al.; U.S. Patent No. 4,476,197 by Herceg; U.S.
Patent No. 4,510,213 by Schnacke; U.S. Patent No.
20   4,476,198 by Ackerman et al.; U.S. Patent No. 4,510,212
by Fraioli; and U.S. Patent No. 4,599,282 by Hirota et
al., the contents of which are hereby incorporated by
reference.

Although fuel cell structures and materials may
25   vary, a fuel cell is basically a galvanic energy
conversion device that chemically combines hydrogen or a
hydrocarbon fuel and an oxidant within catalytic confines
to produce a DC electrical output. In one form of fuel
cell, cathode material defines the passageways for the
30   oxidant, and anode material defines the passageways for
the fuel, and an electrolyte separates the cathode and
anode materials. The fuel and oxidant, typically as
gases, are then continuously passed through the cell
passageways separated from one another, and unused fuel
35   and oxidant discharged from the fuel cell generally also
remove the reaction products and heat generated in the
cell. Being infeeds, the fuel and oxidant are typically
not considered an integral part of the fuel cell itself.

The hydrogen reaction on the anode (the
40   negative electrode) with oxide ions generates water with
the release of electrons, and the oxygen reaction on the

cathode with the electrons, effectively forms the oxide
ions. Electrons flow from the anode through the
appropriate external load to the cathode, and the circuit
is closed internally by the transport of oxide ions

5   through the electrolyte. The electrolyte insulates the
cathode and anode from one another with respect to
electron flow but permits oxygen ions to flow from the
cathode to the anode. Thus, the reactions are as
follows:

10

$$cathode \quad \tfrac{1}{2}O_2 + 2e \rightarrow O^{2-} \tag{1}$$

$$anode \quad H_2 + O^= \rightarrow H_2O + 2e \tag{2}$$
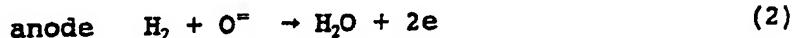
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The overall cell reaction is:

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \tag{3}$$
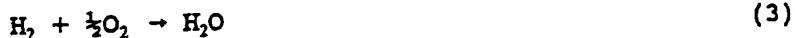
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In addition to hydrogen, the fuel can be
derived from a hydrocarbon such as methane (CH_4) reformed
by exposure to steam at 350°C or above, which initially

25   produces carbon monoxide (CO), and three molecules of
hydrogen. As hydrogen is consumed, the shift reaction
occurs as follows:

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{4}$$

30   The overall reaction of hydrocarbons in the cell is
illustrated by

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{5}$$

35   Inasmuch as the conversion is electrochemical,
the thermal limitations of the Carnot cycle are
circumvented; therefore, efficiencies in the range
exceeding 50% fuel energy conversion to electrical output
can be theoretically obtained. This is much higher than

40   equivalent thermal engines utilizing the same fuel
conversion, including even a conventional diesel powered
engine.
The electrolyte isolates the fuel and oxidant

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gases from one another while providing a medium allowing
the ionic transfer and voltage buildup between the
electrodes. The electrodes (cathode and anode) provide
paths for the internal flow of electrical current within
5   the fuel cell to the cell terminals which also connect
then with an external load. The operating voltage across
each cell is of the order of 0.7 volts maximum so the
individual cells are placed in electrical series to
obtain a convenient load voltage. A series connection is
10 accomplished between adjacent cells with an interconnect
material which isolates the fuel and oxidant gases from
one another while yet electronically connecting the anode
of one cell to the cathode of an adjoining cell.

     Inasmuch as the active electrochemical genera-
15 tion of electricity takes place only across the
electrolyte portions of the fuel cell, any interconnect
separation between the cathode and anode, in order to
provide the series electrical connection between the
cells, renders that part of the fuel cell electrically
20 nonproductive. The percentage of interconnect to
electrolyte wall area defining each cell, if high, could
significantly reduce the energy or power densities of
such a fuel cell.

     Diffusion of the reacting molecular species
25 (fuel or oxidant) through the electrodes to the
electrolyte also limits the cell performance. Fuel and
oxidant must diffuse away from the flow in the respective
passageways through the electrolyte to the reaction
sites. The fuel and oxidant diffuse through the
30 electrodes to the electrolyte and react at (or near) the
three-phase boundary of the gases, the electrodes (anode
or cathode) and electrolyte, where electrochemical
conversion occurs. As the hydrogen partial pressure of
the fuel gases decreases along the length of the fuel
35 passageways, less voltage is generated near or at the
downstream end of the fuel passageways.

     While it is possible thermally and electrically

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to extract great quantities of energy from the fuel, it
is also inherently inefficient to extract such energies
to the complete depletion of the fuel and oxidant.
Complete conversion of the fuel in the fuel cell is thus
5   not sought as it is intrinsically inefficient in the
overall output of the cell voltage. For both a single
cell and cells in gas flow series, the maximum
theoretical voltage decreases along the cell. Practical
fuel cells therefore consume only 80 to 90% of the fuel
10   because the cell voltage decreases rapidly as the
hydrogen becomes less than 5% of the fuel gas. The
reduction in maximum cell voltage as the fuel is consumed
is an important limitation.

One proposed type of solid oxide fuel cell
15   utilizes a ceramic support tube, and the electrodes
(anode and cathode) and electrolyte are built up as
layers on the support tube. The support tube is confined
in a sealed housing, the fuel and oxidant are manifolded
to the housing, and the reaction products are ported from
20   the housing as required. Depending on the layer build-
up, the fuel is either conveyed internally of the support
tube and the oxidant is conveyed externally of the
support tube or vice versa. A practical fuel cell unit
would be composed of many such tubes supported within an
25   exterior housing, and manifolding would separate and
direct the fuel and oxidant proximate the tubes.

A typical support tube might be formed of
calcium stabilized zirconia (ZrO_2 + CaO); the cathode
typically would be applied to the exterior face of the
30   support tube and might be in the form of lanthanum
manganite ($LaMnO_3$); the electrolyte would be layered over
a portion of the cathode, comprised, for example, of
yttria-stabilized zirconia (ZrO + Y_2O_3); and the anode
would be layered over the electrolyte comprised, for
35   example, of a cobalt yttria-stabilized zirconia cermet or
mixture (Co + ZrO_2 + Y_2O_3). The oxidant would thereby flow
internally of the structural tube while fuel will be

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circulated externally of the tube. For part of the cell
where a series connection was to be made with an adjacent
cell, the interconnection would be layered over the
cathode at this location instead of the electrolyte and
5   anode to engage the anode of the adjacent cell. The
interconnect might be comprised, for example, of
lanthanum chromite ($LaCrO_3$).

Electrolytes used in solid oxide fuel cells
must withstand very high temperatures, that is,
10   temperatures from about 700°C to about 1100°C as well as
being an excellent oxygen ion conductor. The less
resistant the electrolyte is to oxygen ion conductivity,
then the more rapidly the oxygen ions are transported and
the more efficient is the generation of electrical
15   energy. Thus, the electrolyte has a significant impact
upon the efficiency of the fuel cell. Electrolytes
typically used in fuel cells are zirconia based inasmuch
as zirconia has generally been preferred for its strength
as well as for having good oxygen ion conductivity.
20   Bismuth oxide, in contrast, has not been utilized in fuel
cells even though it has oxygen ion conductivity which is
many fold that of zirconia under similar conditions.
Bismuth oxide, however, is not readily stable in the pre-
sence of a reducing atmosphere and, once reduced, loses
25   its integrity and conductivity. Thus, bismuth oxide has
not been used to any significant extent in fuel cells.

SUMMARY OF THE INVENTION

30   A graded metal oxide electrolyte comprising
gradations of zirconia and bismuth oxide across the
cross-section of electrolyte has now been invented. A
graded electrolyte having one surface layer rich in
zirconia, that is, at least about 95% zirconia, and an
35   opposed surface layer which is rich in bismuth oxide,
that is, having at least 65% bismuth oxide with
intermediate layers or zones of various zirconia-bismuth
oxide contents has now been invented. The bismuth oxide

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present in the graded electrolyte of the instant
invention is present in combination with yttria (the
molar ratio of bismuth oxide to yttria is about 3 to 2,
plus or minus about 10%). The presence of a small amount
of bismuth oxide in a zirconia-rich layer acts as a
sintering aid.

DESCRIPTION OF FIGURES

FIG. 1 is a sectional view of a typical solid
oxide fuel cell;

FIG. 2 is a sectional view of a graded
electrolyte of the instant invention;

FIG. 3 is a table illustrating various four-
layer composites;

FIG. 4 is a graph comparing the coefficients of
thermal expansion of various $Bi_2O_3/Y_2O_3/ZrO_2$ compositions;

FIG. 5 is a photomicrograph of a cross-section
of a hot-pressed, four-layer composite electrolyte;

FIG. 6 is a schematic illustration of a conduc-
tivity-measuring apparatus used to measure conductivity
of composite electrolyte pellets; and

FIG. 7 is a graph illustrating the conductivity
of a four-layer electrolyte composite of the instant
invention.

DETAILED DESCRIPTION OF INVENTION

A unique electrolyte for solid oxide fuel cells
(SOFCs) has been invented. The unique electrolyte which
has one surface layer rich in zirconia and an opposed
surface layer rich in a bismuth oxide-yttrium oxide
(yttria) composition enables an SOFC to be operated
efficiently at a temperature range of about 600°C to
about 700°C in contrast to about 1000°C to 1100°C for a
fuel cell having a monolithic zirconia electrolyte.
Lower temperature operation is advantageous from the
standpoint of seal life, thermal stresses and the like.

The unique electrolyte of the instant invention

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generally comprises at least three different
compositional zones and preferably four or five
compositional zones wherein the first outer layer is rich
in zirconia preferably containing about at least 95%
zirconia and from about 3% to about 5% of a bismuth
oxide-yttria oxide composition wherein the molar ratio of
bismuth oxide to yttria is about 3:2 plus or minus about
10% and preferably plus or minus about 5%. A second
electrolyte surface layer is rich in bismuth oxide-yttria
composition containing a minimum of about 85% to about
95% of such a bismuth oxide-yttria oxide composition. At
least one intermediate layer between the surface zones is
present wherein the zirconia content and the bismuth
oxide-yttria content are more equally balanced.

A substantial difference exists in the coef-
ficient of thermal expansion between zirconia and a
bismuth oxide-yttria composition. A gradation of
compositional content across the wall thickness of the
electrolyte from a substantially pure zirconia surface
zone to a substantially pure bismuth oxide-yttria surface
zone minimizes the stress at the interfaces between the
various compositional zones. Preferably, about four
compositional zones are present and are generally most
efficient for the purposes of the invention.

The different compositional zones within the
electrolyte are generally of a fuel-side surface zone of
zirconia sintered to a high degree of the theoretical
density. The zirconia-rich surface zone exposed to fuels
must not be pervious or porous inasmuch as the presence
of any fuel, for example, hydrogen or a hydrocarbon such
as methane, propane, or the like, will tend to reduce any
bismuth oxide that it comes in contact with. However,
the other zones may be less dense and may be formed
wherein a skeletal zirconia layer is filled with bismuth
oxide to create a bismuth oxide-rich layer. Skeletal
ceramic articles are described in the U.S. patent
application of Khandkar, U.S. Patent Application No.

346,074, filed May 2, 1989, the text of which is incorporated herein by reference.

A very effective use of this invention resides in making flat or planar electrolytes. These electrolytes may be made by mechanically pressing material in a green state wherein a mold is filled with ceramic powder of preselected compositions to give a graded compositional variation across the thickness of the electrolyte, or the electrolyte may be made from tape cast materials of different compositions which are layered to give the appropriate compositional variation. The tape cast layers may then be pressed together to form the electrolyte in the green state subject to firing at temperatures in the range of about 1100°C to about 1450°C to give a sintered article.

A typical solid oxide fuel cell is illustrated in FIG. 1 where item 10 is the electrolyte, item 11 an electrode (anode) and item 12 is an electrode (cathode). A cathode is generally formed of $LaMnO_3$ or $LaCoO_3$ and is exposed to oxygen or air. The anode is composed of Ni/ZrO_2 cermet and is exposed to fuel which is typically hydrogen or methane. The cell may be operated in reverse to act as an electrolyzer with a mixture of H_2 and water vapor being introduced to the fuel cell and polarity reversed so that a direct current is introduced to create a voltage potential between the two electrodes with the former cathode becoming the anode to cause oxygen ions to migrate from one electrode through the electrolyte to the other electrode. This is done to regenerate fuel in certain instances such as use aboard space vehicles. In space vehicles, solid oxide fuel cells operate not only to produce energy but also to produce potable water. An SOFC employing the electrolytes of the instant invention performs well as an electrolyzer.

A cross-section of a graded electrolyte in accordance with the instant invention is illustrated in FIG. 2. The electrolyte has a plurality of zones with

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zone L1 being an outer layer consisting essentially of zirconia with minor amounts of a sintering aid, for example, up to about 5% bismuth oxide. The opposite outer layer or outer zone L2 consists essentially of bismuth oxide and yttria with minor amounts of zirconia, for example, up to about 10% zirconia. Bismuth oxide and yttria are present in preferably a 3 to 2 molar proportion plus or minus 10%, preferably plus or minus 5%.

Layer L3 is situated adjacent to layer L1 and consists essentially of zirconia as the major component and bismuth oxide as a minor component, bismuth oxide being doped with yttria in a molar ratio similar to layer L2. In layer L3, the zirconia is present from about 65% to 80% and preferably at about 70%. Yttria may be present in conjunction with said zirconia in an amount of about 3 to about 10 mol. % of said $ZrO_2 \cdot Y_2O_3$ composition.

L4 is situated between layers L3 and L2 and consists essentially of bismuth oxide as the major component with zirconia as a minor component. Bismuth oxide is combined with yttria in the ratio set forth for layer L2 with the bismuth oxide-yttria combination being present as about 75% to 85% of the layer and preferably as about 80%, with zirconia making up the remainder.

In the graded electrolyte just described, an electrode is present on the surface of each outer layer. A cathode is affixed to the bismuth oxide-rich layer, that is, layer L2 which is exposed to oxygen or air. Preferably, the cathode material is platinum, lanthanum strontium manganate, lanthanum strontium cobaltite, silver and similar non-reactive, electronic conductive materials. The cathode must generally be porous to permit oxygen molecules to pass through the electrode to be present at the electrode/electrolyte interface whereby oxygen dissociates into oxygen ions which are transported across (through) the electrolyte to combine with fuel at the anode region. Silver cathodes need not be made

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porous inasmuch as silver, at the temperatures of
operation of the cell, generally has high permeability to
oxygen molecules.

At the anode surface, oxygen combines with fuel
such as carbon or hydrogen to form a gaseous reaction
product such as carbon monoxide, carbon dioxide and
water.

Typical overall thicknesses for graded electro-
lytes of the instant invention are from about 0.1 to
about 0.5 mm. The thickness of individual layers may be
from about 0.025 to about 0.1 mm.

The invention may be more fully understood by
reference to the following examples:

Example 1

Preliminary experiments on fabrication of two-
and three-layer composite electrolyte pellets with 8 mol
% yttria-stabilized zirconia and bismuth 0.75, yttria
0.25 oxide (molar ratios) compositions indicated that the
integrity of the pellets was poor. Composite three-layer
pellets fabricated by uniaxial compaction (250 MPa) of 8
mol % yttria-stabilized zirconia (outer layer) and $Bi_{0.75}$
$Y_{0.25}$ oxide containing 5% (outer layer) and 41% zirconia
(interior layer) resulted in delamination between the
three layers which had been individually pressed and then
pressed together to form a single pellet in method A.
The composite pellets were sintered together at 1100°C.
Using method B, the three powder compositions were
uniaxially pressed to a pressure of 70 MPa and sintered
to 1100°C for one hour. It was noticed that while
bonding between the three layers improved, there seemed
to be some volatility of the bismuth oxide phase as
evidenced by the extensive coloration of the furnace
setters as well as the "pitted" appearance of the
pellets. Sintered pellets exhibited a maximum weight
loss for the bismuth-rich compositions of about 1.5%.

In the two- and three-layer composites sintered

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at 1100°C, there was delamination evident in each of the
samples. At a lower sintering temperature of 800°C,
there was generally better integrity of the composite
structures, however, the zirconia layer at such sintering
5   temperature exhibited about 24% porosity.

This suggests that the primary reason for
delamination is due to generation of interfacial thermal
stresses due to differences in sinterability of the two
phases as well as the thermal expansion coefficient
10   mismatch. Those stresses may be due to differences in
densification rates and temperatures between the
zirconia-rich phase and the bismuth oxide-rich phases.

15   Example 2

To lower the CTE (coefficient of thermal expan-
sion) mismatch, four-layer composite electrolytes with
compositions as given and illustrated in the table in
20   FIG. 3 were fabricated. The CTEs of the different oxide
compositions are shown in FIG. 4. Stabilized zirconia
has a CTE of approximately 11×10^{-6}/°C while $Bi_{0.75}Y_{0.25}$ oxide
solid solution has a CTE of 15.5×10^{-6}/°C and $Bi_{0.6}Y_{0.4}$ has a
CTE of 12.5×10^{-6}. Increasing the zirconia content of a
25   Bi_2O_3/Y_2O_3 composition lowers its CTE.

The zirconia-rich compositional layer contained
5 mol % of the bismuth oxide-yttria oxide solid solution.
Prior earlier work indicated such a solid solution (Bi_2O_3
Y_2O_3) acted as a sintering aid for the zirconia. In the
30   work of Keizer et al., it was demonstrated that it is
possible to sinter high zirconia content compositions to
densities greater than 95% of theoretical with the pre-
dominant phase assemblage comprising high conductivity
cubic crystals and minor amounts of the second phase
35   present mainly at the grain boundaries. This latter
phase was determined to be predominantly bismuth oxide
rich and was presumed to form a liquid phase with good
wetting characteristics which promoted diffusion and thus
aided sintering.

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Comparison of sintered composite pellets
between 4L-1, 4L-2, 4L-3 series (see FIG. 3) indicated
that the optimal composition is the four-layer
composition with $Bi_{0.6}Y_{0.4}$ as the best solid solution. An
example of 4L-3 sintered at 800°C for two hours generally
showed no evidence of delamination at the interfaces.
However, some problems associated with concavity of the
composite as well as incomplete densification of zirconia
layer existed.

A sample of the 4L-3 composition was hot
pressed as an alternative method for simultaneously
achieving optimal density of the zirconia-rich outer
layer and good adhesion between the layers with reduced
shrinkage stresses. The hot pressing temperature range
was from about 850°C to about 1100°C at a pressure of
about 1 to about 10 ksi.

Several trials were made to optimize the hot
pressing parameters using various ramp rates, pressures
and soak times as well as die materials. In most cases,
the hot pressed samples cracked through the bismuth
oxide-rich layers, that is, layers 2, 3 and 4. Finally,
hot pressing in air was accomplished successfully on
small, approximately 0.5 inch diameter, composite pellets
using an alumina die and punch set. FIG. 5 shows the
micrographs of such a hot pressed 4L-3 composite
electrolyte. This sample was sintered at 1100°C for one
hour. This particular composite pellet exhibited the
best interfacial characteristics and the highest density
in the zirconia-rich layer.

Example 3

The conductivity of four-layer composite
electrolytes (sample 4L-3) was determined.

A schematic of the experimental setup used to
measure conductivity of electrolyte pellets is
illustrated in FIG. 6. The apparatus consisted of an
alumina tube onto which the composite electrolyte pellets

were sandwiched between alumina media to effect good
contact with silver leads. Silver metal leads were taken
out through vertical slots made on the side of the tube.
Silver paste was applied on to the faces of the pellets

5   to maintain good contact and the pellets were sandwiched
between silver foil. The entire arrangement was placed
inside a quartz tube which was sealed with provisions for
controlled gas atmospheres. In some cases, conductivity
was determined over four decades of frequency ranging

10   from 5Hz to 50KHz.

FIG. 7 shows the typical conductivity plot of a
composite electrolyte having the composition 4L-3. The
conductivity degraded somewhat with decreasing
temperature and was somewhat less than a pure solid

15   solution. The conductivity was still greater than that
of stabilized zirconia by a factor of five.

One of the unique aspects of composite electro-
lytes of this invention is that a solid state, planar
fuel cell/electrolyzer may be constructed. For space

20   applications, fuel cells are often linked with
electrolyzers so that in one mode oxygen and hydrogen, or
other hydrogen- containing gas such as methane, are
reacted in the fuel cell to produce electricity and water
vapor, while in an electrolyzer, water may be introduced

25   as water vapor be to electrolyzed to regenerate fuel,
that is, hydrogen and oxygen.

The composite electrolyte of the instant
invention permits the construction of a single fuel
cell/electrolyzer unit to perform both functions. The

30   composite electrolyte permits operation at a lower
temperature, for example, in the neighborhood of 700-
800°C, as opposed to about 1000°C for a zirconia
electrolyte-based fuel cell. The increased conductivity
of the composite electrolyte permits operation at the

35   lower temperatures which enables the use of metals and
metal-containing materials such as perovskites and the
like as electrodes, conductors and the like thereby

simplifying construction of the cell. Examples of such
electrode materials are doped $LaMnO_3$, $LaCoO_3$, Pt or Ag as
the cathode, $NiZrO_2$, $CoZrO_2$, Pt or Ag as the anodes.

For example, in space applications, a fuel cell
is operated to generate electricity. During times when
electricity may be generated from solar panels and the
like, an electrolyzer enables the operator to regenerate
the fuel to later be used in the fuel cell. Thus, the
electrolyzer and fuel cell are rarely operated
concurrently and a combination of these units into a
single unit does not detract from the operation of the
space vehicle.

Because of the different temperatures of
sintering and different coefficients of thermal expansion
between pure bismuth oxide or a bismuth oxide/yttria
solid solution and zirconia, many of the composite
electrolytes prepared exhibit some delamination between
layers or unacceptable porosity of the zirconia-rich
outer layer or some dishing, that is, curvature of the
electrolyte plate due to the difference in coefficient of
thermal expansion which ultimately tends to shrink
bismuth oxide-rich layers to a smaller planar dimension
than the zirconia oxide-rich outer layer.

Some of these problems may be eliminated or at
least diminished by first pressing a powder composition
at a low pressure, for example, about 20 MPa, then
introducing the second layer and similarly pressing that
and so on until a three- to four-layer composite of
powder has been formed, then subjecting the whole
composite to pressure in the neighborhood of about 200
MPa. Such a composite planar material may then be hot
pressed at about 1073K to about 1273K to form an article
having minimum porosity, minimum delamination and maximum
planarity. Forming composites with five to six layers
may also tend to eliminate delamination problems and
result in less warpage.

Another approach towards forming planar

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sintered composite electrolytes is to form both outer
layers of thin zirconia-rich materials, gradually grading
the composition towards a relatively thick center layer
which is bismuth oxide rich. Fuel cells in which bismuth
5   oxide is used as any part of the electrolyte must
eliminate the possibility of fuel, for example, hydrogen,
reaching the bismuth oxide and causing it to reduce,
thereby greatly decreasing its oxygen ion-conducting
property. Zirconia, however, may be exposed to either
10   oxygen or fuel without any adverse consequence.

The thickness of the outer layers of a sym-
metrically graded electrolyte is from about 10 to about
20 μm. Interior layers may have a thickness from about
50 to about 75 μm with the overall thickness of the
15   electrolyte being from about 75 μm to about 100 μm.

Another advantage of using such a symmetrical
graded electrolyte, i.e. one in which both outer layers
are zirconia, is that no care need to be taken as to
which surface is in contact with the electrode or the
20   cathode. A graded electrolyte of such construction can
be made from individual tape cast layers of different
compositions or by placing zirconia powder in an
isostatic press and then pressing to about 20 to 30 MPa.
A powder composition containing 30 to 40% bismuth oxide
25   and the remainder of zirconia can then be sequentially
placed in the press and similarly pressed. The internal
bismuth oxide-rich layer is preferably thicker than the
combined zirconia layers. Another intermediate layer may
be used in which the bismuth oxide predominates or a
30   central layer in which bismuth oxide is present as 82% to
95% of the powder. The whole composition may then be
uniaxially pressed to a very high pressure, for example,
in the neighborhood of 200 MPa. Such a composition may
then be hot pressed quickly at high temperatures, for
35   example, temperatures in the range of 1300°C since the
bismuth oxide is fully contained, except for the edges,
so that very little loss of bismuth oxide occurs. Also,

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if the hot pressing is done rapidly, substantially
complete sintering of the zirconia layers may occur and
because of the insulating characteristics of the ceramic,
the bismuth oxide interlayer may not achieve the same

5   temperature as the surface layers, that is, bismuth oxide
may only reach a lower temperature which is quite satis-
factory to sinter completely the bismuth oxide. Such a
sintered composite electrolyte may then be cooled in a
standard fashion without any significant delamination

10   occurring, however, the composite electrolyte may be
removed from the furnace and the sintered surface layers
uniformly rapidly cooled to shrink the surface layers
while the central regions are still relatively warm so
that when the central regions cool and shrink, the

15   relative shrinkage of the central region to the surface
layers will, in fact, be less so that less delamination
occurs. Also, by processing in this fashion, the article
in actual use at a temperature of 700-800°C should be at
a relatively neutral stress condition. Any surface

20   cooling must be carefully done to avoid uneven surface
temperatures which would set up undesirable thermal
stresses.

            Composite electrolytes according to this
invention have low resistance to oxygen transport and

25   generally have conductivities which are a factor of five
or more greater than zirconia and, when formed in a
symmetrical pattern as described herein, the
conductivities may be as high as even ten times that of
zirconia. In symmetrical formation, the relative

30   thickness of the zirconia may be very small in comparison
to the bismuth oxide-rich central zone so that the bulk
of the electrolyte is formed of a material having a high
oxygen ion conductivity.

CLAIMS

What is Claimed:

1.   An oxygen conducting ceramic electrolyte
having a graded composition comprising:
a first outer surface layer comprising Bi_2O_3 as the
         predominant metal oxide and an effective
         electrolytic metal oxide dopant which increases
         the oxygen ion transport characteristics of
         said Bi_2O_3;
a second outer surface layer comprising ZrO_2 as the
         predominant metal oxide and an effective
         electrolytic metal oxide dopant which increases
         the oxygen transport characteristics of ZrO_2;
         and
at least one intermediate layer comprising Bi_2O_3 in a
         significant amount and an electrolytic dopant
         for Bi_2O_3, and ZrO_2 in a significant amount and
         an effective electrolytic dopant for ZrO_2, said
         Bi_2O_3 being present in an amount substantially
         less than the amount of Bi_2O_3 present in said
         first outer surface layer and said ZrO_2 being
         present in an amount substantially less than
         the amount of ZrO_2 present in said second outer
         surface layer.

2.   A solid state fuel cell/electrolyzer
comprising:
a composite sintered electrolyte having a first outer
         layer consisting essentially of ZrO_2, Y_2O_3 or
         CeO_2 with a second outer layer consisting
         essentially of Bi_2O_3 and a suitable metal oxide
         dopant and with one or more inner layers having
         compositions intermediate said outer layers;
a first porous electrode adherent to said first outer
         layer, said electrode being suitable for

contact with a gaseous fuel containing
hydrogen;

a second electrode which is porous or pervious to oxygen
molecules, said second electrode adherent to
said second outer layer;

5

means to heat said electrolyte to a temperature of about
700-800°C;

conductor means to conduct current to or from said
electrodes;

10

containment means for containing the respective gases in
contact with their respective electrodes and
insulated from one another;

gaseous fuel introduction means for introducing fuel to
said first electrode; and

15

oxygen introduction means for introducing oxygen to said
second electrode.

3. A sintered ceramic article of a graded
composition comprising:

20

a first outer layer consisting essentially of about 95%
zirconia and about 5% of an oxide mixture of
Bi_2O_3 and Y_2O_3 wherein the molar ratio of Bi_2O_3 to
Y_2O_3 is from about 3:1 to about 3:2 and wherein
said zirconia is substantially present as cubic

25

zirconia;

a second outer layer consisting essentially of an oxide
mixture of Bi_2O_3 and Y_2O_3 wherein the molar ratio
of Bi_2O_3 to Y_2O_3 is from about 3:1 to about 3:2;
and

30

at least two intermediate layers wherein a first
intermediate layer adjacent said first outer
layer consists essentially of about 65-80% ZrO_2
and about 20-35% of an oxide mixture of Bi_2O_3
and Y_2O_3 wherein the molar ratio of Bi_2O_3 to Y_2O_3

35

is from about 3:1 to about to about 3:2 and a
second intermediate layer adjacent said second
outer layer and in contact with said first

19

intermediate layer, said second intermediate
layer consisting essentially of about 15-25%
ZrO_2 and about 75-85% of an oxide mixture of
Bi_2O_3 and Y_2O_3 wherein the molar ratio is from

5   about 3:1 to about 3:2, said layers forming an
integral unit.

4.   A process for forming a sintered ceramic
article of a graded composition comprising:

10   forming a first outer layer consisting essentially of
about 95% zirconia powders and about 5% of a
powder mixture of Y_2O_3 and a sufficient amount
of a bismuth compound which converts upon
sintering to Bi_2O_3 to be present in a ratio of

15   Bi_2O_3 to Y_2O_3 of from about 3:1 to 3:2;
forming a first intermediate layer in intimate contact
with said first outer layer, said first
intermediate layer consisting essentially of
about 75-95% of ZrO_2 powders and about 5-25% of

20   a powder mixture of Y_2O_3 and a sufficient amount
of a bismuth compound which converts upon
sintering to Bi_2O_3 to be present in a ratio of
Bi_2O_3 to Y_2O_3 of about 3:1 to 3:2;
forming a second intermediate layer in intimate contact

25   with said first intermediate layer consisting
essentially of about 35-45% ZrO_2 and about 55-
65% of a powder mixture of Y_2O_3 and a sufficient
amount of bismuth compound which converts upon
sintering to Bi_2O_3 to be present in a ratio of

30   Bi_2O_3 to Y_2O_3 of about 3:1 to 3:1;
forming a second outer layer consisting essentially of a
powder;
pressing said layers together to form a green ceramic
article; and

35   hot pressing said green ceramic article at a sufficient
temperature and at a sufficient pressure to
form a sintered article.

20

5.   The electrolyte of Claim 1, wherein said
first outer layer comprises at least 95% by weight of a
Bi_2O_3-metal oxide dopant composition.

5   6.   The electrolyte of Claim 2, wherein said
metal oxide dopant is one selected from a group
consisting essentially of rare earth oxides such as
yttria, ytterbia, or alkaline earth oxides such as calcia
or magnesia.

10

7.   The electrolyte of Claim 1, wherein said
second outer layer comprises at least 95% by weight of a
ZrO_2-metal oxide dopant composition.

15   8.   The electrolyte of Claim 7, wherein said
metal oxide dopant is one selected from the class
consisting essentially of yttria, ytterbia, calcia,
magnesia, scandia or other alkaline earth or rare earth
oxides.

20

·9.   The electrolyte of Claim 1, wherein two
intermediate layers are present, a first intermediate
layer comprising predominantly a Bi_2O_3-metal oxide dopant
composition and a minor amount of a ZrO_2-metal oxide
25   dopant composition adjacent said first outer layer, a
second intermediate layer comprising predominantly a ZrO_2-
metal oxide dopant composition and a minor amount of a
Bi_2O_3-metal oxide dopant composition adjacent said second
outer layer and said first intermediate layer.

30

10.   The electrolyte of Claim 9, wherein said
first intermediate layer comprises at least about 75% by
weight of a $Bi_2O_3 \cdot Y_2O_3$ composition, wherein said $Bi_2O_3 \cdot Y_2O_3$
molar ratio is from about 3:1 to about 3:2.

35

11.   The electrolyte of Claim 9, wherein said
second intermediate layer comprises at least about 65% by

weight of a $ZrO_2 \cdot Y2O_3$ composition wherein said Y_2O content
is from about 3 to about 10 mol. % of said $ZrO_2 \cdot Y_2O_3$
composition.

5   12.   The sintered ceramic article of Claim 3,
wherein said molar ratio of Bi_2O_3 to Y_2O_3 is about 3:2.

           13.   The sintered ceramic article of Claim 3,
wherein said first intermediate layer is from about 80-
10   85% ZrO_2.

           14.   The process of Claim 4, wherein said hot
pressing is conducted at a pressure of about 1 to about
10 ksi and a temperature of about 850°C to about 1100°C
15   for a period of time sufficient to sinter said first
outer layer to at least 95% of theoretical density.

           15.   An oxygen-conducting ceramic electrolyte
in a sintered condition having a graded composition
20   comprising:
a pair of thin outer layers consisting essentially of
           zirconia as the predominant metal oxide and
           effective electrolytic dopant which increases
           the oxygen transport characteristics of said
25   zirconia; and
at least one central layer consisting essentially of Bi_2O_3
           in a significant amount in conjunction with an
           effective electrolytic dopant for said Bi_2O_3 and
           a significant amount of ZrO_2 in conjunction with
30   an effective electrolytic dopant for said ZrO_2.

           16.   The electrolyte of Claim 15, wherein said
outer layers are sintered to a density of at least about
95% of theoretical.

35

           17.   The electrolyte of Claim 15, wherein said
dopant for said ZrO_2 consists of Y_2O_3, Yb_2O_3, CaO.

18. The electrolyte of Claim 15, wherein said dopant for said Bi_2O_3 consists of Y_2O_3, Yb_2O_3.

19. The electrolyte of Claim 15, wherein said central layer is thicker than the combined thicknesses of said outer layers.

20. The electrolyte of Claim 15, wherein said central layer is predominantly Bi_2O_3 with an intermediate layer of Bi_2O_3/ZrO_3 between the central layer and each of said outer layers, the composition of said intermediate layer being intermediate of the composition of said central layer and said outer layers.
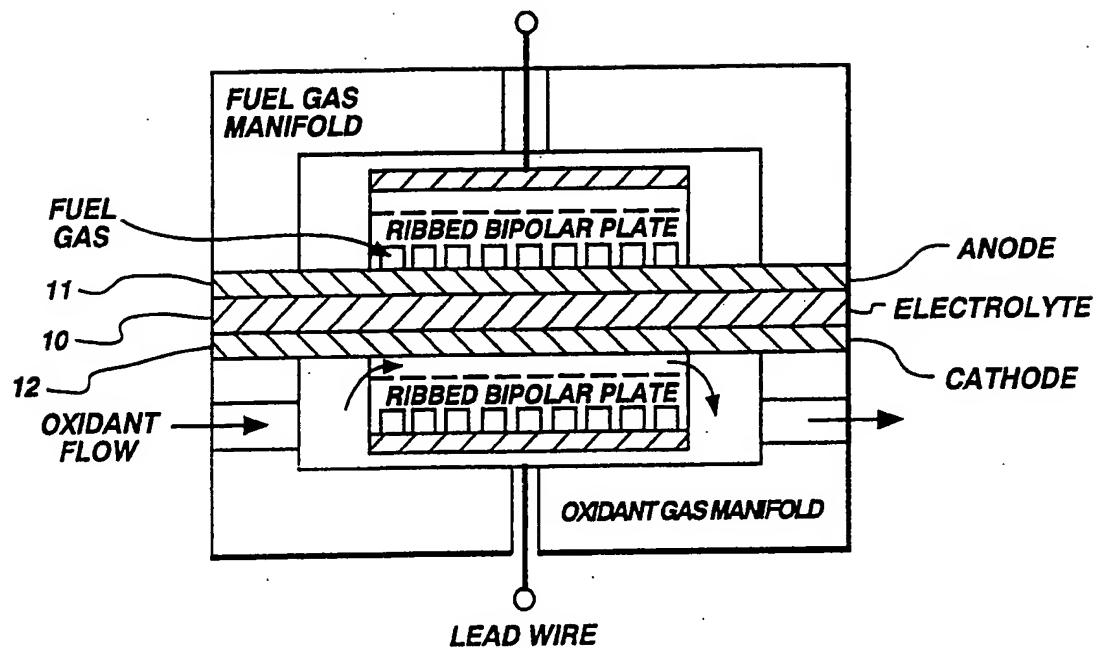
PLANAR CONFIGURATION
SOLID OXIDE FUEL CELL

FIG. 1

ELECTRODE

L2	Bl_2O_3 RICH LAYER WITH DOPANTS

L4	$Bl_2O_3 + ZrO_2$ (MINOR) WITH DOPANTS

L3	$ZrO_2 + Bl_2O_3$ (MINOR) WITH DOPANTS

L1	ZrO_2 RICH LAYER WITH DOPANTS

ELECTRODE

Fig. 2

CTE PROPERTIES AND COMPOSITIONS OF 4-LAYER ELECTROLYTES

LAYER	COMPOSITION	CTE (x 10 E6/C)	SAMPLE CODE
1 (ZrO_2 RICH)	95% ZrO_2 + 5% $Bi_{0.75}Y_{0.25}$	10.4	4L-1
2	80% ZrO_2 + 20% $Bi_{0.75}Y_{0.25}$	10.4	
3	40% ZrO_2 + 60% $Bi_{0.75}Y_{0.25}$	11.7	
4 (Bi_2O_3 RICH)	100% $Bi_{0.75}Y_{0.25}$	15.5	
1 (ZrO_2 RICH)	85% ZrO_2 + 15% $Bi_{0.75}Y_{0.25}$	10.9*	4L-2
2	31% ZrO_2 + 69% $Bi_{0.75}Y_{0.25}$	14.1*	
3	7% ZrO_2 + 93% $Bi_{0.75}Y_{0.25}$	15.5	
4 (Bi_2O_3 RICH)	100% $Bi_{0.75}Y_{0.25}$	15.5	
1 (ZrO_2 RICH)	95% ZrO_2 + 5% $Bi_{0.6}Y_{0.4}$	10.7	4L-3
2	80% ZrO_2 + 20% $Bi_{0.6}Y_{0.4}$	10.9*	
3	40% ZrO_2 + 60% $Bi_{0.6}Y_{0.4}$	13.1	
4 (Bi_2O_3 RICH)	100% $Bi_{0.6}Y_{0.4}$	15.5	

Fig. 3

**THERMAL EXPANSION OF Bi(1-x)Y(x)-ZrO2 COMPOSITIONS**
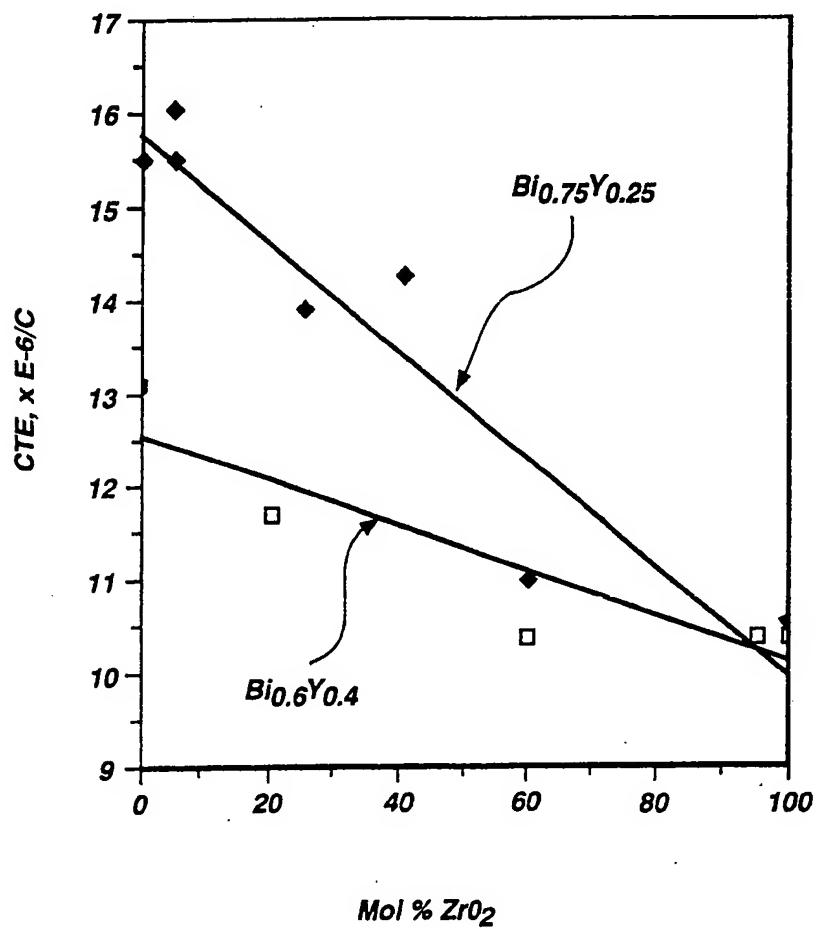
Fig. 4

LAYER 1 | LAYER 2

FIG 5
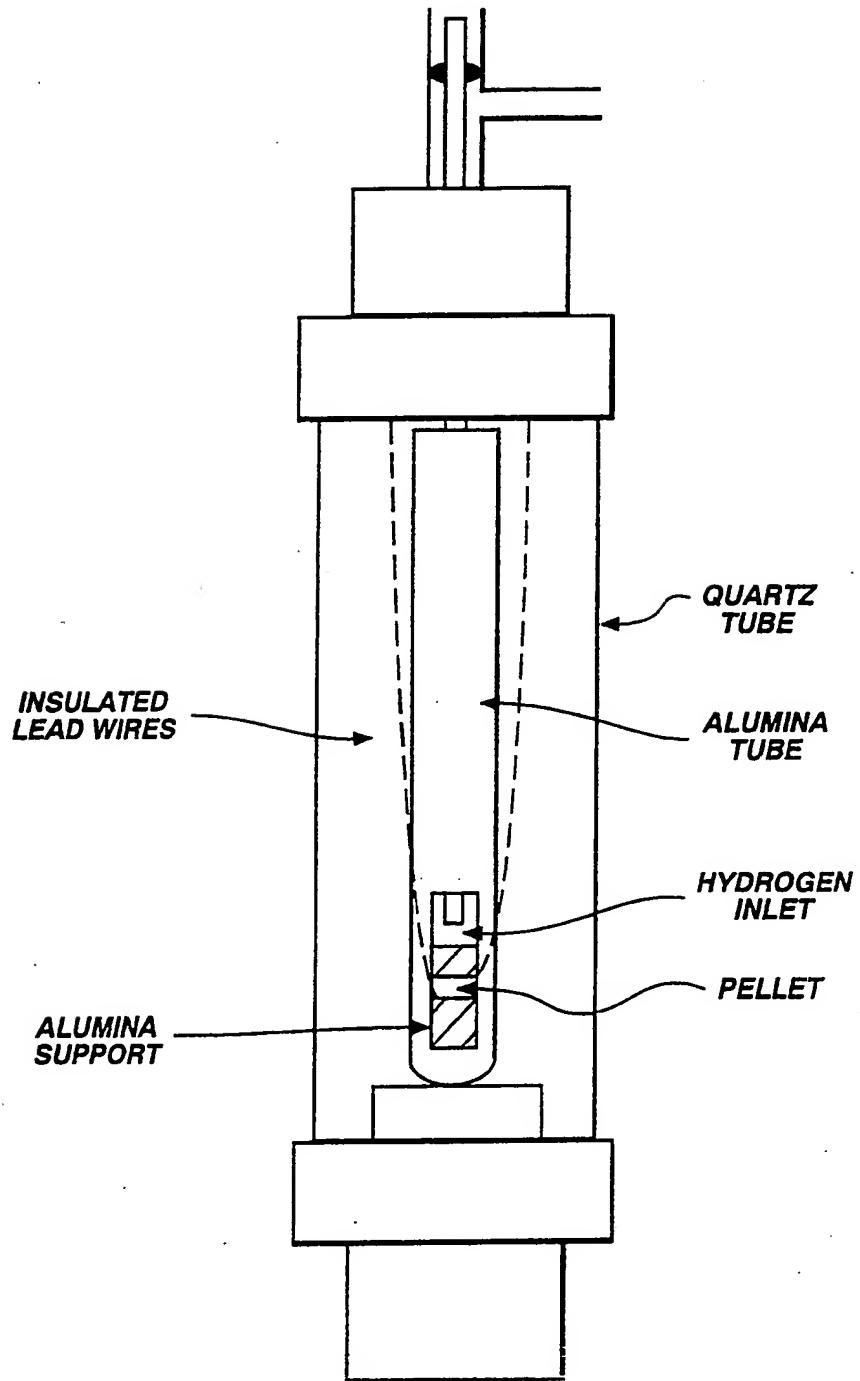
SCHEMATIC OF A CONDUCTIVITY RIG

Fig. 6

TYPICAL CONDUCTIVITY OF COMPOSITE ELECTROLYTE
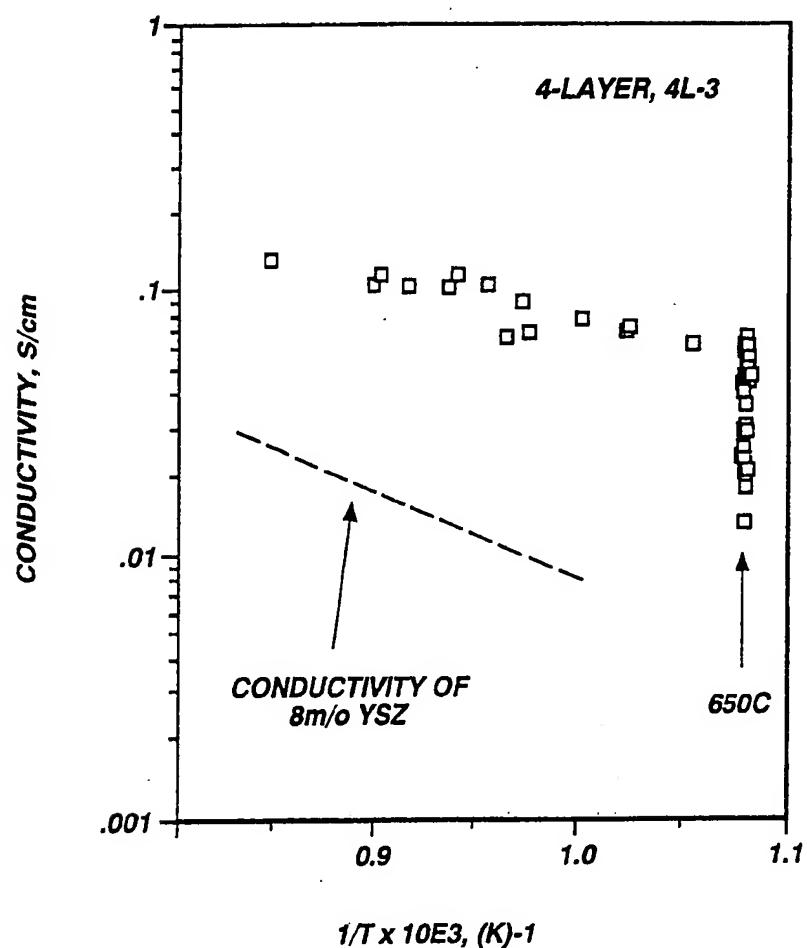
Fig. 7
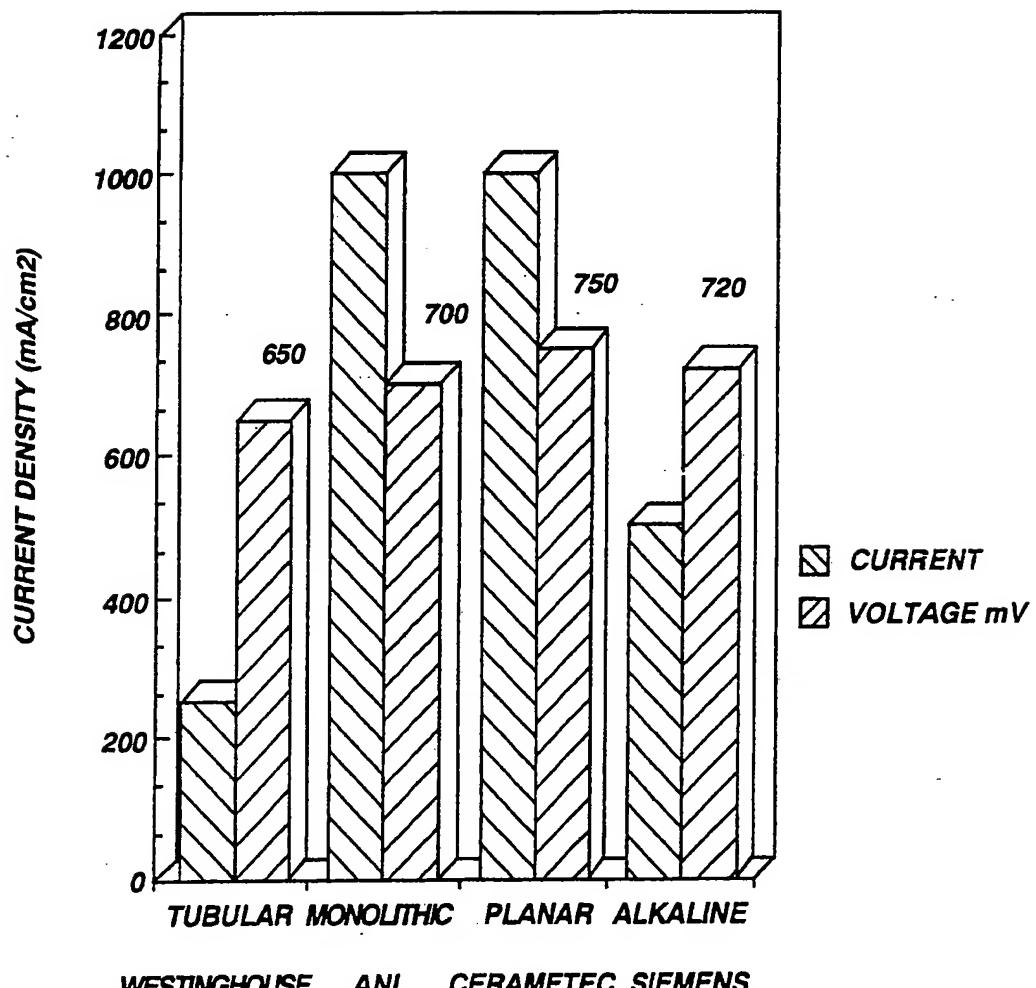
COMPARISON OF FUEL CELL PERFORMANCE

Fig. 8